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CLAIMS

- 1. The use of an organosilyl ester of a carboxylic, sulphonic or phosphoric acid as an alkaline hydrolysis or erodability booster for the binder system of a paint formulation.
- 2. The use according to claim 1, wherein more than one silylester of a carboxylic, sulphonic or phosphoric acid are used in any such paint formulation ie. a mixture of such silylesters are utilised as boosters.
- 3. The use according to claim 1 or 2, wherein the carboxylic, sulphonic or phosphoric acid part of the organosilylester has a non-vinylic alpha carbon.
- 4. The use according to any of claims 1-3, wherein the binder system comprises a film forming binder.
- 5. The use according to any preceding claim, wherein the organosilylester of the invention is also independently film forming.
- 6. A film or resinous binder for a paint composition comprising organosilylesters of carboxylic, sulphonic or phosphoric acid, said acid having a non-vinylic alpha carbon and being other than rosin.
- 7. The use of organosilylesters of monocarboxylic, sulphonic or phosphoric acids, said acids having a non-vinylic alpha carbon and being other than rosin as a binder component of a paint binder system.
- 8. A paint composition comprising organosilylesters of monocarboxylic, sulphonic or phosphoric acids, said acids having a non-vinylic alpha carbon and being other than rosin.
- 9. A paint according to claim 8, wherein the paint comprises a binder system, the said binder system comprising the said organosilylesters of monocarboxylic, sulphonic or phosphoric as a binder component.
- 10. A paint composition comprising silylesters of monocarboxylic,
 sulphonic or phosphoric acid other than rosin as a binder component
 of the binder system.

- 11. A use, binder or paint composition according to any preceding claim, wherein there are mixtures of organosilyl esters of carboxylic, sulphonic or phosphoric acids.
- 12. A process for preparing a paint composition characterised in that one step of the process is the addition of a binder component comprising organosilylesters of acids other than rosin as a binder component of the binder system.
- 13. A process for preparing a paint composition according to claim 12, wherein the paint is an antifouling paint.
- 10 14. A use, process, binder or paint composition according to any preceding claim, wherein the organosilyl ester of the carboxylic, sulphonic or phosphoric acid is based on a hydrocarbyl residue of greater than or equal to C3.
 - 15. A use, process, binder or paint composition according to any preceding claim, wherein the organosilyl ester of the acid is represented by the general formula (I):

$$R^{7} - Z = \begin{pmatrix} R^{4} & R^{1} \\ Si - L' & R^{3} \\ R^{5} & R^{3} \end{pmatrix}$$
(I)

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wherein Z represents:

wherein each R⁴ and R⁵ may be hydroxyl or may be independently selected from alkyl, aryl, alkoxyl, aryloxyl, -L'-SiR¹R²R³, -L'-(SiR⁴R⁵L')_n-

SiR¹R²R³, -L'-SiR¹R²-, -L'-(SiR⁴R⁵L')_n-SiR¹R²-, alkenyl, alkynyl, aralkyl or aralkyloxyl radicals optionally substituted by one or more substituents independently selected from the group comprising alkyl, alkoxyl, aralkyl, aralkyloxyl, hydroxyl, aryl, aryloxyl, halogen, amino (preferably, tertiary amino) or amino alkyl radicals, or R⁴ or R⁵ may independently be an –O-Z-R⁸ group, wherein R⁸ is defined as R⁷ below;

wherein each R¹, R² and R³ may independently represent hydrogen, hydroxyl, alkyl, alkenyl, alkynyl, alkoxyl, aryl, aryloxyl, aralkyl or aralkyloxyl radical optionally substituted by one or more substituents independently selected from the group comprising alkyl, alkoxyl, aralkyl, aralkyloxyl, aryl, aryloxyl, halogen, hydroxyl, amino (preferably, tertiary amino) or amino alkyl radicals, or R¹, R² or R³ may independently be an – O-Z-R⁸ group,

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L' represents O, S, or NR⁶, where R⁶ is defined as is R⁹ below,

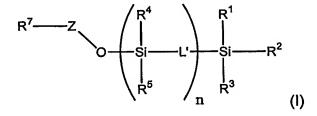
each n independently represents a number of $-Si(R^4)(R^5)-L'$ - groups from 0 to 1000,

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wherein R^7 is an aralkyl, aryl, alkenyl, alkynyl, or a C_2 or higher alkyl group optionally substituted, in the case of the hydrocarbyl radicals with one or more substituents selected from the equivalent substituents as defined for R^1 , R^2 , R^3 , R^4 and R^5 above.

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16. A process for producing a silyl ester of formula (I)



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wherein Z represents:

wherein each R⁴ and R⁵ may be hydroxyl or may be independently selected from alkyl, aryl, alkoxyl, aryloxyl, -L'-SiR¹R²R³, -L'-(SiR⁴R⁵L')_n-SiR¹R²R³, -L'-SiR¹R²-, -L'-(SiR⁴R⁵L')_n-SiR¹R²-, alkenyl, alkynyl, aralkyl or aralkyloxyl radicals optionally substituted by one or more substituents independently selected from the group comprising alkyl, alkoxyl, aralkyl, aralkyloxyl, hydroxyl, aryl, aryloxyl, halogen, amino (preferably, tertiary amino) or amino alkyl radicals, or R⁴ or R⁵ may independently be an –O-Z-R⁸ group, wherein R⁸ is defined as R⁷ below;

wherein each R¹, R² and R³ may independently represent hydrogen, hydroxyl, alkyl, alkenyl, alkynyl, alkoxyl, aryl, aryloxyl, aralkyl or aralkyloxyl radical optionally substituted by one or more substituents independently selected from the group comprising alkyl, alkoxyl, aralkyl, aralkyloxyl, aryl, aryloxyl, halogen, hydroxyl, amino (preferably, tertiary amino) or amino alkyl radicals, or R¹, R² or R³ may independently be an – O-Z-R⁸ group,

L' represents O, S, or NR⁶, where R⁶ is defined as is R⁹ below,

each n independently represents a number of –Si(R⁴)(R⁵)-L'- groups from 0 to 1000,

wherein R^7 is an aralkyl, aryl, alkenyl, alkynyl, or a C_2 or higher alkyl group optionally substituted, in the case of the hydrocarbyl radicals with one or more substituents selected from the equivalent substituents as defined for R^1 , R^2 ,

R³, R⁴ and R⁵ above with the proviso that when R⁷ is an alkenyl or alkynyl it does not include a vinylic alpha carbon;

by reaction of a higher boiling acid of formula (II)

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wherein Z and R⁷ are as described above;

with a silyl ester of a lower boiling acid of formula (III)

$$\begin{array}{c|c}
O & R^4 & R^1 \\
\hline
R^9 & R^5 & R^3
\end{array}$$
(III)

wherein R¹, R², R³, R⁴, R⁵, L['] and n are defined above except where R¹, R², R³, R⁴or R⁵ are an —O-Z-R⁸ group in formula I they may be replaced by an -O-Z-R¹⁰ group in formula III;

wherein R^9 is defined as R^7 above except R^9 may also be hydrogen or C_1 alkyl and with the proviso that the acid of the ester formed by R^9 (R^9 ZOH) boils at a lower temperature than the acid R^7 ZOH of formula (II);

wherein R10 is defined as R^7 above except R^{10} may also be hydrogen or C_1 alkyl and with the proviso that the acid of the ester formed by R^{10} (R^{10} ZOH) boils at a lower temperature than the acid R^7 ZOH of formula (II);

while removing the formed acid group of formula (IV) and/or (V)

R⁹ZOH (IV)

R¹⁰ZOH (V)

- from the system to produce at least one protected acid group of said formula (I).
 - 17. A use, process, binder or paint composition according to claim 15 or 16, wherein when an acylated silyl ester is formed in accordance with formula I it has more than one acyloxy group attached to one or several silicon atoms.
- 18. A use, process, binder or paint composition according to any of claims 15-17, wherein the carboxyl radical part of formula (IV) is selected from formyl, acetyl, propionyl and butyryl.
- 19. A use, process, binder or paint composition according to any of claims
 15-18, wherein examples of the carboxyl radical part of formula R⁷ZOH
 may independently include but are not limited to propionyl, butyryl,
 pivaloyl, oxaloyl, malonyl, succinyl, glutaryl, adipoyl, benzoyl, phthaloyl,
 isobutyroyl, sec-butyroyl, octanoyl, isooctanoyl, nonanoyl, isononanoyl,
 abietyl, dehydroabietyl, dihydroabietyl, naphthenyl, anthracenyl, abietyl
 dimer (Dymerex®), fully hydrogenated dihydroabietyl (Foral®) and the
 like and polymers or copolymers thereof.
- 20. A use, process, binder or paint composition according to any of claims 16-19, wherein examples of the organosilylated carboxylate compounds of general formula (III) include but are not limited to trimethylsilylformiate, dimethylsilyldiformiate, methylsilyltriformiate, tri-n-butyl 1,-acetoxy-silane, di-n-butyl 1,1-diacetoxy-silane, n-butyl 1,1,1-triacetoxy-silane, tri-n-propyl-l-acetoxy-silane, di-n-propyl 1,1-diacetoxy-silane, n-propyl 1,1,1-triacetoxy-silane, tri-isopropyl-l-acetoxy-silane, tri-isobutyl-l-acetoxy-silane, tri-methyl-l-acetoxy-silane, di- methyl 1,1-diacetoxy-silane, methyl 1,1,1-triacetoxy-silane, triethyl- l-acetoxy-silane, vinyl 1,1,1-triacetoxy-silane, tribenzyl- l-acetoxy-silane, triamyl- l-acetoxy-silane, triphenyl- l-acetoxy-silane, trimethylsilylpropionate, t-

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butyldimethylsilylacetate, pentamethyl-l-acetoxy-disiloxane, heptamethyll-acetoxy-trisiloxane, nonamethyl-1-acetoxy-tetrasiloxane, nonaethyl-1acetoxy-tetrasiloxane, nona-t-butyl-1-acetoxy-tetrasiloxane, nonabenzyl-1-acetoxy-tetrasiloxane, nona-isopropyl-1-acetoxy-tetrasiloxane, nona-npropyl-1-acetoxy-tetrasiloxane, nona-isobutyl-1-acetoxy-tetrasiloxane. nona-amyl-1-acetoxy-tetrasiloxane, nona-n-butyl-1-acetoxy-tetrasiloxane, nona-dodecyl-1-acetoxy-tetrasiloxane, nona-hexyl-1-acetoxytetrasiloxane, nona-phenyl-1-acetoxy-tetrasiloxane, nona-octyl-1-acetoxytetrasiloxane, undecamethyl-1-acetoxy-pentasiloxane, undecaethyl-1acetoxy-pentasiloxane, undeca-t-butyl-1-acetoxy-pentasiloxane, undecabenzyl-1-acetoxy-pentasiloxane, undeca-isopropyl-1-acetoxypentasiloxane, undeca-n-propyl-1-acetoxy-pentasiloxane, undecaisobutyl-1-acetoxy-pentasiloxane, undeca-amyl-1-acetoxy-pentasiloxane, undeca-n-butyl-1-acetoxy-pentasiloxane, undeca-dodecyl-1-acetoxypentasiloxane, undeca-hexyl-1-acetoxy-pentasiloxane, undeca-phenyl-1acetoxy-pentasiloxane, undeca-octyl-1-acetoxy-pentasiloxane tridecamethyl-1-acetoxy-hexasiloxane, tridecaethyl-1-acetoxyhexasiloxane, trideca-t-butyl-1-acetoxy-hexasiloxane, tridecabenzyl-1acetoxy-hexasiloxane, trideca-isopropyl-1-acetoxy-hexasiloxane, tridecan-propyl-1-acetoxy-hexasiloxane, trideca-isobutyl-1-acetoxyhexasiloxane, trideca-amyl-1-acetoxy-hexasiloxane, trideca-n-butyl-1acetoxy-hexasiloxane, trideca-dodecyl-1-acetoxy-hexasiloxane, tridecahexyl-1-acetoxy-hexasiloxane, trideca-phenyl-1-acetoxy-hexasiloxane, trideca-octyl-1-acetoxy-hexasiloxane.

- 21. A use, process, binder or paint composition according to any of claims 16-20, wherein the organosilylated carboxylate compounds of general formula (III) are selected from ethyl triacetoxy silane, vinyltriacetoxy silane, dimethyldiacetoxy silane and trimethylsilylacetate.
- A use, process, binder or paint composition according to any of claims 15
 -21, wherein examples of higher boiling acids which can be silylated to produce the silylesters of the present invention include acids of C₃ and above ie. aliphatic acid homologues greater than or equal to propionic

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acid such as C4-C60 acids e.g. isostearic acid; cyclic aliphatic acids such as naphthenic acid; and C4 – C60 acids (including aromatic or unsaturated acids) such as hydrogenated rosin.

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- 23. A use, process, binder or paint composition according to any preceding claim, wherein the co-binders which may be used in combination with the silylester of the invention may be selected from :
 - Resinates of Ca, Cu or Zn

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- Naphthenates of Ca, Cu, Zn
- Vinyls like Laroflex MP (commercially available from BASF)
- Acrylates like Neocryl B725 (commercially available from Avecia)
 Cu/Zn/Ca acrylates, e.g. as described in EP 342276; EP 982324
 (Kansai) or polyesters e.g. as described in EP 1033392 (Kansai);
 Tri-organosilyl(meth)acrylates copolymers as described e.g. in EP
 131626 (M&T); US 4593055 (M&T); EP 775773 (Chugoku); EP
 646630 (NOF); US 5436284 (NOF); WO 0162811 and WO 0162858
 (SIGMA COATINGS);
 Hydrophilic (meth) acrylates such as e.g. described in FR 2 557 585
 - 24. A use, process, binder or paint composition according to claim 23, wherein the co-binders which may be used in combination with the silylester of the invention are selected from tri organo silyl(meth) acrylate copolymers.

(Jotun), EP 526441 and EP 289441 (SIGMA COATINGS).

25. A use, process, binder or paint composition according to claim 24, wherein the binders incorporate polyfunctional acids such as poly(silylesters) or Dymerex ® to help improve the film forming properties of the binder.